



When Semiconductors Go Nano

At the nanoscale, silicon, germanium, and diamond take on unexpected characteristics.

WE all know diamonds, or we think we do. Diamonds are a girl's best friend, sang Marilyn Monroe in the movie *Some Like it Hot*. They appear on many a third finger, brilliantly faceted and sparkling. On a more practical note, because diamonds are one of the hardest substances on Earth, the industrial sector makes extensive use of them.

Who would suspect then that the most miniscule bit of diamond, just a few

hundred atoms, would take on the exotic shape of a fullerene or buckyball at the surface? At the nanoscale—a nanometer is a billionth of a meter or 1,000 times smaller than the diameter of a human hair—materials behave differently than they do in their larger, bulk form. In this size regime, the laws of quantum mechanics predominate.

Yet the recent revelation that the outer surface of a molecule of diamond, a

nanodiamond, is shaped like a soccer ball came as a real surprise. The discovery was made by a Livermore team that for the first time computationally modeled nanodiamonds to determine their optical properties. They had previously modeled two similar semiconductor materials, silicon and germanium, and expected about the same results.

Physicist Giulia Galli, who leads Livermore's Quantum Simulations Group,

says, “At the nanoscale, the surface of silicon and germanium rearranges its atomic geometry in a way that somehow compresses the core of the nanostructure.” To their amazement, the team found that nanodiamond expands, with a crystalline diamondlike core and a fullerene-like structure around it at the surface.

The first fullerene was a 60-atom carbon buckyball. Livermore’s simulations are the first to reveal bucky diamonds, a new family of carbon clusters. The discovery of the bucky diamond was just one recent finding by a research team led by Galli and Tony van Buuren, an experimental physicist. The team performs quantum molecular simulations and scrutinizes materials experimentally as they seek to better understand the properties of the semiconductor materials silicon, germanium, and diamond at the nanoscale. As part of the Group IV series of elements on the periodic table, these three materials share some interesting properties, as described in the [box on p. 10](#).

According to physical chemist Lou Terminello, materials program leader for the Defense and Nuclear Technologies Directorate, Livermore research on semiconductor nanostructures—also known as nanodots or quantum dots—is

aimed primarily at using them in detectors to reveal the presence of biological or chemical warfare agents. A protein added to the surface of one of these nanoparticles would change when exposed to a biological agent, serving as an indicator.

At the nanoscale, silicon and germanium emit light when stimulated. Nanodiamond, which has more recently come under the microscope, may also change its optical properties as a function of size. In bulk form, all three semiconductors are compatible with biological materials and so could easily be linked with a protein. Whether this biocompatibility still exists when the semiconductors are reduced to the nanoscale remains to be determined. If these nanosemiconductors are indeed biocompatible, their optical, or light-emitting, properties could be exploited to detect specific molecules.

Other uses for light-emitting semiconductor nanoparticles include photonic switches, tunable lasers, and nanocrystal solar cells. Terminello adds, “Quantum dots will likely be some of the next-generation materials for targets at the National Ignition Facility.” By starting with nanostructures, scientists could dictate the target’s precise design. Atom by atom, they could gradually build up

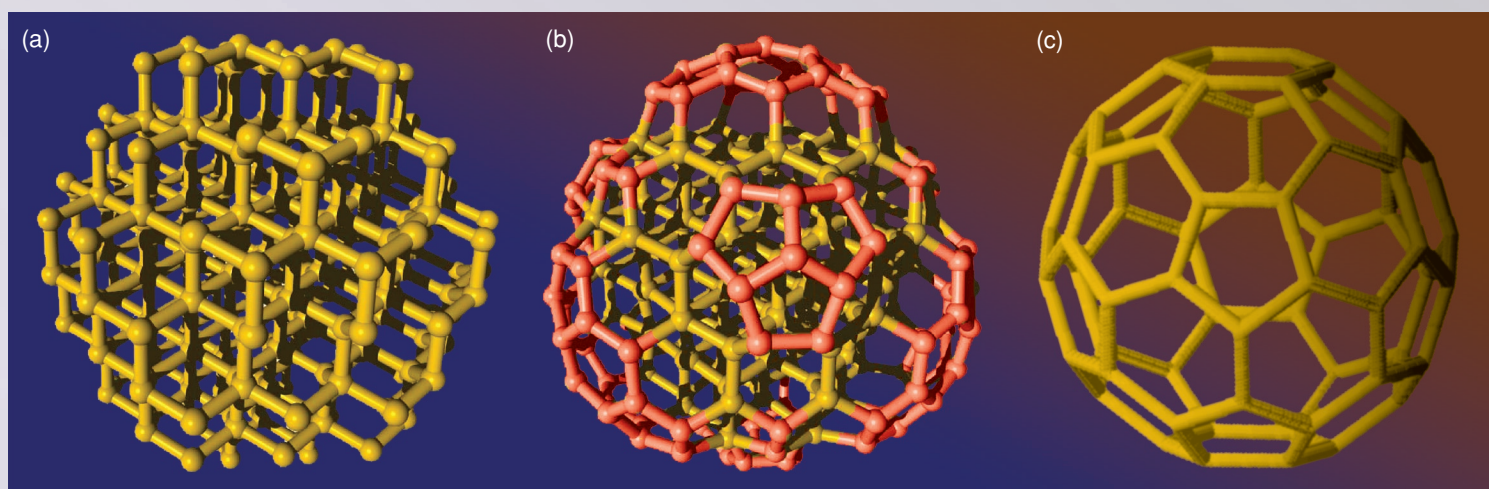
the targets in size from the nanoscale to macroscopic structures.

Nanoscience—the study of the very small—is fundamental to U.S. research. Funding by the U.S. government for nanoscience and nanotechnology is higher than ever, just behind defense spending and funding for biological research. Before tiny bits of any material can be put to use, their unique properties must be better understood. As the recent discovery of the bucky diamond illustrates, the world of Group IV semiconductor nanostructures is still a mystery.

Small Size, Big Change

Reducing any piece of material from a chunk that we might recognize to the nanometer scale changes virtually all of its most basic properties in a fundamental way. Its shape and crystalline structure change, as do its melting and boiling temperatures. Its magnetic properties may be different at the nanoscale. Its optical and electronic properties also change.

In a nanosemiconductor, an effect known as quantum confinement occurs when electrons and “holes” in the material are confined. (A hole is the absence of an electron; the hole behaves as though



Fullerenes, or buckyballs, are soccer-ball-shaped molecules named for R. Buckminster Fuller, whose popular geodesic dome is structurally similar to a fullerene molecule. In first-principles simulations of nanodiamond, (a) the surface of a 1.4-nanometer nanodiamond with 275 atoms spontaneously rearranges itself into (b) a fullerene at about 300 kelvins. These carbon clusters have a diamond core (yellow) and a fullerene-like reconstructed surface (red). (c) A classic 60-atom carbon buckyball.

it were a positively charged particle.) Typically, quantum confinement causes the material's optical gap—the energy difference between filled states and empty states—to widen. A larger optical gap prompts dramatic changes in electronic and optical properties. Bulk silicon when stimulated does not emit visible light, but in 1990, researchers found that nanoparticles of silicon do.

Livermore researchers and others have since determined that silicon nanoparticles emit different colors of light depending on their diameter. In 1997, germanium nanoparticles were found to emit light. In the last two years, other Livermore scientists have discovered that the optical gap of nanodiamond does not change until its size is reduced to less than 2 nanometers.

Nanoparticles are also different from the bulk form of the material in that the percentage of atoms at or near the surface of the particle is far greater. The surface of nanoparticles thus plays a large role in determining the particle's electronic and optical properties.

It Started with Silicon

Livermore's first work with Group IV semiconductor nanostructures took place in the mid-1990s. The photoluminescence of

silicon had only recently been discovered, indicating that this element might be a promising material for optical applications.

Livermore researchers used a gas-phase vaporization process, in which melted silicon was heated and vaporized in the presence of a buffer gas, to synthesize silicon particles ranging from 1 to 6 nanometers. Numerous production techniques exist, but most of them allow only limited size control of the resulting particles. They also produce particles with a specific surface chemistry that is less useful for investigations of precise electronic structure.

Either hydrogen or oxygen was then bonded to the surface of the tiny molecules to "passivate" the dangling bonds of highly reactive silicon. Using spectroscopic and x-ray absorption techniques to probe the particles' characteristics, the Livermore team was the first to measure the band edges of the optical gap of silicon and to determine that the gap changes as the nanoclusters become smaller. These findings clearly indicated the importance of the quantum confinement effect on the optical properties of silicon nanoclusters.

Subsequent fine-tuning of the synthesizing process made it possible to produce silicon nanoclusters in an even

narrower distribution of sizes (± 7 percent of average size) as measured using an atomic force microscope. Work in the late 1990s definitively correlated quantum confinement changes as a function of the size of silicon nanoparticles, in agreement with quantum confinement theory.

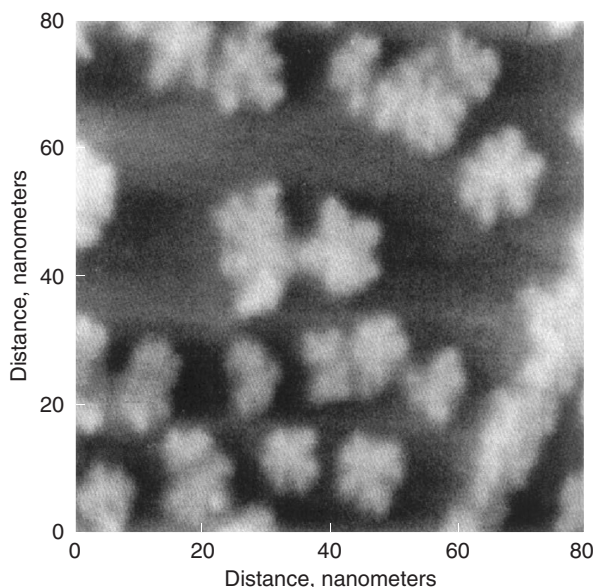
As Livermore and other research institutions worldwide experimented further with semiconductor nanoclusters, their potential uses as biological markers and nanostructure lasers became more evident. With increased concerns about bioterrorism, van Buuren and Galli obtained funding from the Laboratory Directed Research and Development Program to develop atomically controlled nanostructures for biowarfare detectors. Their team, composed of researchers from the Physics and Advanced Technologies and the Chemistry and Materials Science directorates, is relatively large. As interest in all things nano has burgeoned, the number of nanoscience experts at Livermore has grown.

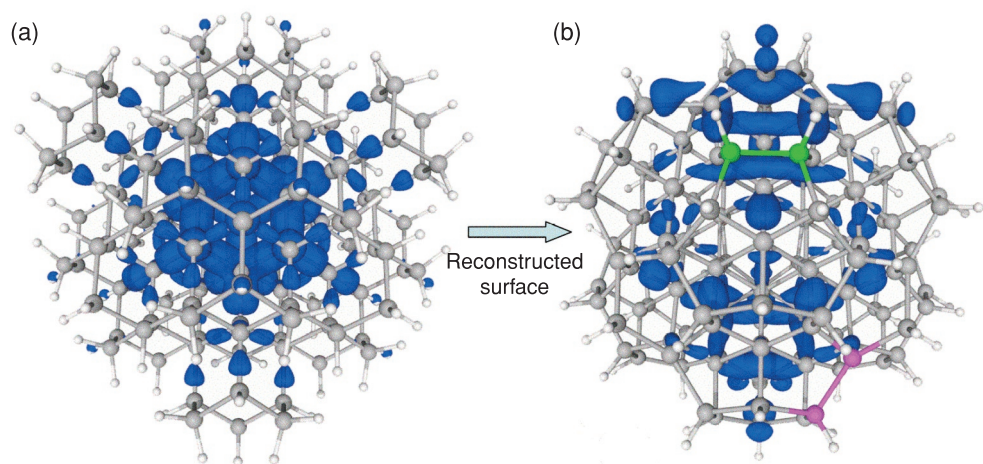
Simulations Verify and Surprise

The traditional purpose of computerized simulations of physical phenomena is to verify experimental findings. But simulations can also go where an experiment cannot. This is especially true for examining the surface of nanoclusters. The effects of quantum confinement on semiconductor nanodots can be obtained experimentally; however, the changes in the properties of the comparatively large surface area of a nanostructure are difficult to determine in experiments. First-principles simulations, which do not contain any input from experimental data, are a valuable tool for discovering the dependence of a nanostructure's optical and mechanical properties on its surface structure.

Using Livermore's massively parallel supercomputers, Galli's group has undertaken several computational studies of the surface chemistry of Group IV semiconductor nanoclusters. An early

An image of silicon nanocrystals using an atomic force microscope. The nanocrystals, produced using gas-phase vaporization, range from 1 to 4 nanometers. Note how the nanoclusters gather at the step edges of the graphite substrate or assemble into snowflakelike superclusters.





(a) The “idealized” structure of a 1.8-nanometer silicon nanodot. When the molecule is removed from a larger piece of bulk silicon, each silicon atom is ideally terminated with a hydrogen atom. (b) But at the nanoscale, the molecule instead reconstructs. Its electronic properties change considerably, increasing the optical gap.

study used density functional theory and quantum Monte Carlo codes to perform first-principles calculations of the surfaces of silicon nanoclusters. The group examined the effect of replacing one or more atoms of a hydrogen-passivated silicon nanocluster with other passivants. A remarkable change results when just two hydrogen atoms are replaced by more reactive oxygen atoms. The electron charge cloud is drawn toward the oxygen atom, dramatically changing the optical properties of the silicon dot.

From these and many similar calculations, the group has concluded that quantum confinement is only one mechanism responsible for a semiconductor’s light-emitting properties. For example, they have confirmed experimental findings by researchers outside the Laboratory that oxygen passivation of silicon dots reduces their optical gap while hydrogen passivation increases it.

A recent study modeled spherical silicon clusters ranging from 53 to 331 atoms (0.7 to 2.0 nanometers), the largest nanoparticles ever studied with the highly accurate quantum Monte Carlo technique. A team examined the

process of surface reconstruction—in which unstable dangling bonds on a nanoparticle’s surface spontaneously rearrange themselves—and its effects on the particle’s optical properties. In this study, the team found that reconstruction of the surface of silicon nanostructures could have the effect of compressing the nanoparticle. “Time and again, we have found that the specific surface chemistry must be taken into account if we want to quantitatively explain

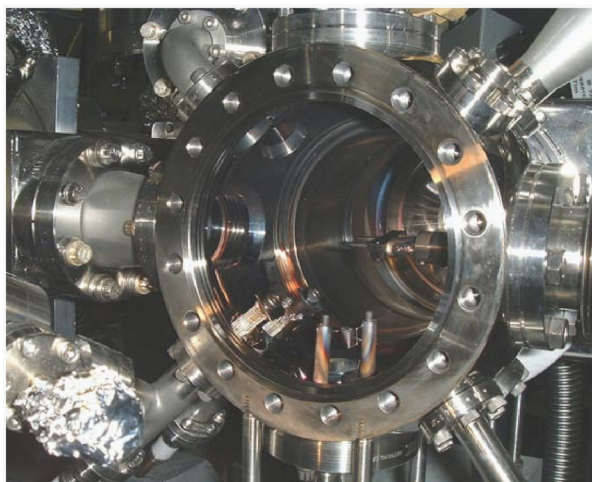
the optical properties of semiconductor nanoparticles,” says Galli.

Germanium Joins the Fray

Although germanium was used extensively in early semiconductor devices, it has since been displaced by silicon as the substrate for most devices. But the 1997 discovery that nanodots of germanium emit light sparked a new interest in this element.

While he was at Livermore as a graduate student of the University of Hamburg, Germany, physicist Christoph Bostedt improved Livermore’s earlier vaporization chamber for synthesizing semiconductor nanoparticles. Among the many modifications he made, the chamber can now synthesize nanoparticles composed of virtually any element. Using this chamber, Bostedt found that by varying preparation parameters, he could dictate the size of the resulting germanium particles.

Now a Livermore postdoctoral fellow, Bostedt is using synchrotron radiation at Lawrence Berkeley National Laboratory’s Advanced Light Source (ALS) for photoemission spectroscopy and x-ray absorption studies of the electronic microstructure of germanium nanocrystal films. “Using ALS, we have produced spectra for germanium that are some of the best obtained anywhere,” he says.



Livermore’s latest gas-phase chamber for synthesizing nanosemiconductors is portable so that nanodots can be prepared and deposited in situ. This gas-phase condensation technique works for virtually all elements, is ultra clean, and produces a wide range of sizes of nanocrystals whose surface chemistry can be manipulated.

Most recently, his team has shown in experiments with ALS that quantum confinement effects are greater in germanium nanocrystals than in silicon nanocrystals for particles smaller than 2 nanometers. The strong confinement they observed and the fast opening of the optical gap—which translate into a highly “tunable” material—indicate germanium nanocrystals would be especially useful in detectors and optoelectronic applications that require extreme sensitivity.

In the theoretical community, others have made similar predictions about the quantum confinement of germanium versus silicon, although considerable controversy

exists. The Livermore team is the first to make this discovery experimentally using thin films of germanium nanocrystal, finding that the behavior of germanium nanocrystals is as sensitive to changes at the surface as silicon. “We believe that disagreements between our experimental results and some theoretical predictions are due to the structural details of the nanocrystals,” says Bostedt. “The structure, especially at the surface, of nanocrystals cannot be ignored.”

Theoretical models that do not use sophisticated quantum simulations typically use idealized nanocrystals isolated in space and not resting on any

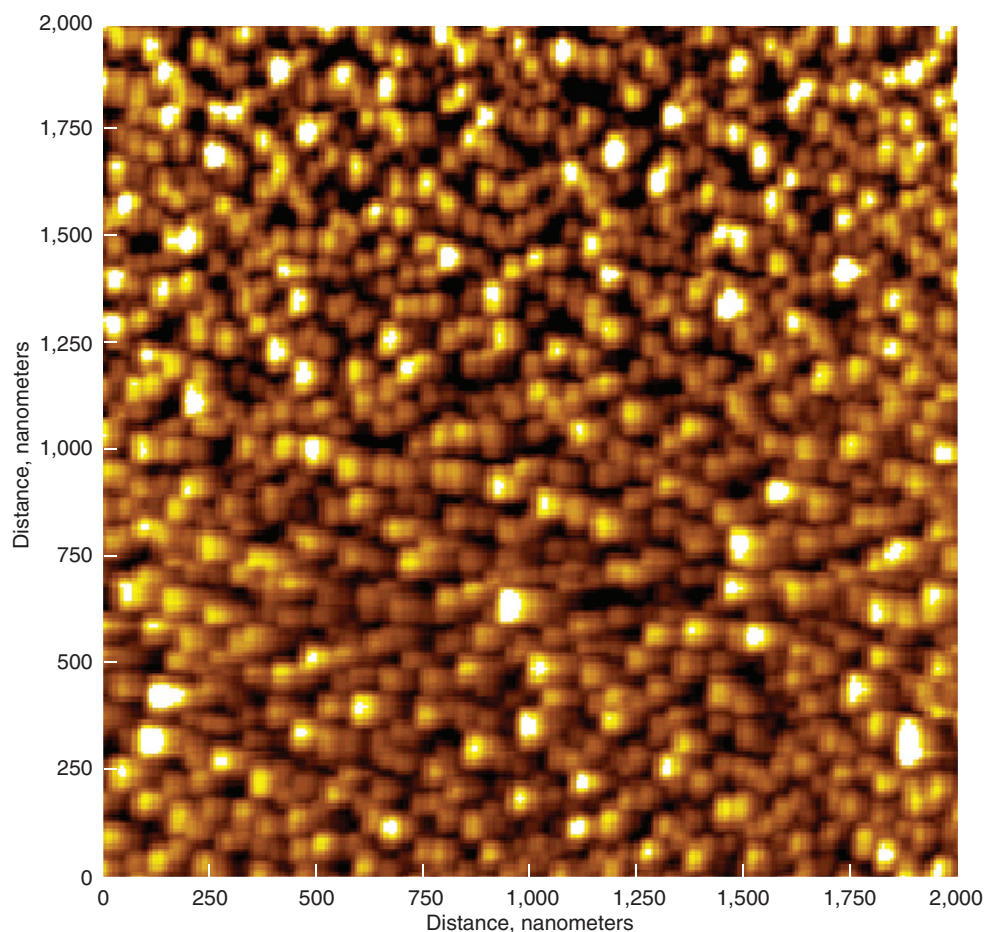
surface. The nanodot’s atomic structure is almost always ignored as well. In contrast, a quantum Monte Carlo investigation at Livermore into the structure and stability of germanium nanoparticles revealed the key role that structure plays. The simulations team found that the surface of germanium nanodots reconstructs when their diameters are smaller than 2.5 to 3 nanometers, a geometric rearrangement that agrees with the Laboratory’s photoemission experiments at ALS.

The Surprising Nanodiamond

Nanodiamond, the most recent Group IV semiconductor to be examined at Livermore, offers plenty of surprises. Livermore is one of the few research groups in the world to perform quantum simulations of nanodiamond behavior.

Livermore data show that the size of nanodiamond must be reduced to less than 2 nanometers before its optical gap increases beyond that of the bulk form. This behavior differs dramatically from that of silicon and germanium where quantum-confinement effects persist in particles of up to 6 and 7 nanometers. These results came from both computer simulations and x-ray absorption and emission experiments using ALS and the Stanford Synchrotron Radiation Laboratory. Both studies aimed to derive a structural model for nanodiamond.

The bucky diamond appeared during calculations of surface reconstruction of 1.4-nanometer diamond particles, which Galli performed with physicist Jean-Yves Raty of Livermore and the University of Liege, Belgium. These simulations started with bare, unpassivated nanodiamond. At low temperature, the bucky diamond reconstruction occurred spontaneously. The first faceted layer took on the properties of graphite, which was followed by the formation of pentagons linking the graphene fragments with atoms underneath. This change made the surface increasingly curved, eventually resulting in an arrangement like half of



Most applications using nanomaterials will require thick films of nanocrystals, such as these germanium nanodots shown under an atomic force microscope.

a 60-atom carbon molecule, the classic buckyball. Simulations showed similar results for surface reconstructions of 2- and 3-nanometer clusters.

These results point yet again to the importance of nanoparticle surfaces. “When the calculations and measured spectra of nanodiamonds are compared,” says van Buuren, “it becomes clear that the surface reconstruction identified by computer simulations is consistent with the features observed in absorption spectra.”

Nanodiamond is interesting because it has been found in meteorites, interstellar dusts, and protoplanetary nebulae, and it appears in residues of detonation. (Nanoparticles of diamond for Livermore experiments are obtained through synthesis from detonation.) And regardless of whether they come from meteorites or detonation, most nanodiamond particles fall in the 2- to 5-nanometer range. Other nanomaterials display a much wider range of sizes even at this small scale.

Raty and Galli used computational methods to explore the causes for this size limitation. The team found that at about 3 nanometers—and for a broad range of pressure and temperature conditions—particles with bare, reconstructed surfaces become thermodynamically more stable

than those with hydrogenated surfaces, and hydrogenation prevents the formation of larger grains.

Prediction Is the Goal

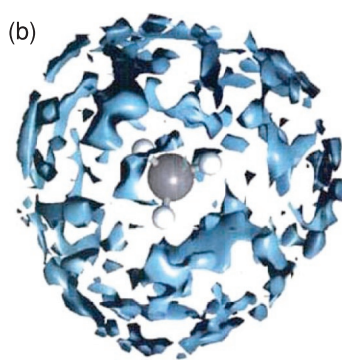
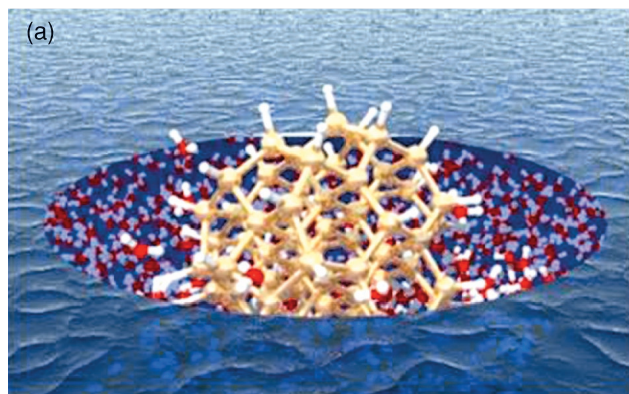
“Understanding how size and surface affect optical and electronic properties is what our research is all about,” says van Buuren. Experimentalists and quantum simulation experts are working together to establish a basic knowledge of the structure and optical properties of semiconductor nanostructures. Their goal is to match these two sets of data and form an ability to predict the characteristics of nanoparticles. Someday, a scientist will know exactly how to produce a nanowidget to detect a deadly pathogen. Perhaps the widget must emit blue light, and the scientist will know that using a nanoparticle of a given size and density produces the desired wavelength.

In the meantime, moving toward that goal, Livermore researchers are beginning to observe the interaction among nanostructures. One team recently performed quantum simulations of the interplay of silicon quantum dots, an inorganic material, and organic molecules, which will be essential in a semiconductor biodetector. In particular, investigators simulated what occurs when organic molecules are attached to silicon quantum

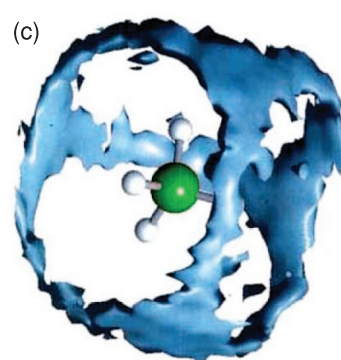
dots. They found that the probability of attaching an organic molecule to a nanodot is greatly increased if light shines on the nanodot, a result that agrees with recent experimental findings by others. Their simulations also indicated a way to select silicon quantum dots with a specific optical gap at the same time that organic molecules are being attached.

Next on Bostedt’s agenda is to make thick films on which germanium particles are closer together and touching, which is how they will be in real-world applications. Unfortunately, when they touch, nanosemiconductor particles tend to lose some of their special electronic properties. Bostedt has developed a surface passivation technique that keeps the particles isolated, reducing the effect of touching. Further experiments will examine the interface where interactions occur between passivated layers to determine what happens to the electronic properties of the entire device.

Others on the team are starting simulations and experiments to explore the structural and optical properties of silicon and germanium nanoparticles in solution. A new two-step cluster aggregation source is under development that will allow for wet chemical modification of the surface of crystalline



Methane



Silane

(a) Simulation of a silicon nanostructure in water. (b) and (c) Monte Carlo simulations from first principles of nanodiamond precursors in water. Both (b) methane and (c) silane are forms of carbon and are hydrophobic; that is, they repel water, just as oil repels water. Although the methane and silane are similar structurally, they interact with water quite differently.

The Periodic Table of Semiconductors

A semiconductor is a crystalline solid that in its pure form exhibits a conductivity midway between that of metals and insulators. The three semiconductor materials that Livermore is studying for possible use as sensors and detectors are silicon, germanium, and diamond. Silicon accounts for almost 99 percent of all commercial semiconductor products. Germanium became famous when the transistor was invented but has since been replaced largely by silicon. Diamond, a monocrystal of carbon, has the physical properties of a wide-optical gap semiconductor, but current technologies do not allow its use as a semiconductor.

These three materials comprise some of the Group IV elements on the periodic table, as shown below. Tin, the fourth potential semiconductor material in this group, has the physical properties of a semiconductor at low temperatures but at room temperature behaves like a metal. These four materials are elemental semiconductors.

Elements in Groups II and VI and in Groups III and V are often combined to form compound semiconductors. Gallium–arsenide

is a typical Group III/V compound semiconductor often used in microwave devices and optoelectronics. Most experiments designed to explore the optical properties of semiconductor nanoclusters have focused on such Group II/VI compound semiconductors as cadmium–selenium.

In contrast, the synthesis of covalently bonded nanoparticles such as silicon has proven to be much more challenging. Silicon and other Group IV semiconductor elements are thus much less well characterized than Group II/VI compounds, and the interplay of quantum confinement and surface properties is less clear. Yet silicon is the preferred material for biomarkers because of its compatibility—at least in its bulk form—with biological materials. Silicon nanoclusters could also be integrated with existing silicon technologies to create nanoscale optoelectronic devices. Germanium and nanodiamond have been studied much less than silicon, but their intriguing characteristics inspire hope that they may be useful as well.

I	II	III	IV	V	VI	VII	VIII
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
	Magnesium	Aluminum	Silicon	Phosphorus	Sulfur		
	Zinc	Gallium	Germanium	Arsenide	Selenium		
	Cadmium	Indium	Tin	Antimony	Tellurium		

silicon nanoparticles produced in the gas phase. This work is a major step toward producing silicon nanoparticles that are useful for biological applications.

As the world faces ever-changing threats and often-unseen enemies, research that enhances our ability to respond is critical. With this research on nanosemiconductors for use in biodetectors, Livermore brings its unique computational and experimental expertise to bear on an issue of extreme importance.

—Katie Walter

Key Words: biodetector, buckyball, germanium, nanocluster, nanocrystal, nanodiamond, nanoparticle, nanoscale, nanoscience, nanotechnology, quantum dot, quantum molecular simulations, semiconductor, silicon.

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